Relating Ocean Optics to Photochemical Transformations of Chromophoric Dissolved Organic Matter (CDOM) in Coastal Waters

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LONG-TERM GOALS

The long-term goal of this research is to use remotely sensed and *in situ* ocean optical data together with photochemical rate determinations to estimate the spatial and temporal significance of photochemistry to marine organic carbon transformations and optical changes (loss of chromophoric/coloured dissolved organic matter: CDOM) resulting from these processes.

OBJECTIVES

Our main objective has been to examine quantitatively the links between optical measurements and photochemical carbon transformations in the sea. Specific objectives have been (1) to collect new UV/VIS optical data, (2) to produce new photochemical efficiency data for CDOM fading and CO_2 production, (3) to consolidate new data with our previous results while ensuring the quality of all, (4) to establish accurate, robust algorithms for the estimation of UV optical properties from remotely sensed water-leaving visible radiance, and (5) to use UV optical properties derived from remote sensing to calculate photochemical reaction rates in the surface ocean, specifically for the production of CO and CO_2 and the loss of CDOM (and consequent changes in UV/Vis attenuation).

APPROACH

Achieving the objectives stated above requires a wavelength dependent description of the *in situ* optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of CDOM. Our general approach uses three connected principles:

(1) There are strong relationships between water-leaving radiance in the visible (412 nm) and diffuse attenuation of UV radiation (323 nm, 338 nm, and 380 nm) (Johannessen et al., 2002).
(2) CDOM is the dominant contributor to the absorption and attenuation of UV in coastal waters and diffuse attenuation of UV can be related directly to its absorption (Johannessen et al., 2002).
(3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores (i.e. CDOM fading) and production of lower-molecular weight compounds. Wavelength-dependent apparent quantum yields (AQYs) for these transformations can be determined experimentally.

Given measurements of solar radiation and upwelling radiance at the sea-surface, we estimate photochemical losses of surface-layer CDOM by applying empirical relationships between: (1)

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14. ABSTRACT
The long-term goal of this research is to use remotely sensed and in situ ocean optical data together with photochemical rate determinations to estimate the spatial and temporal significance of photochemistry to marine organic carbon transformations and optical changes (loss of chromophoric/coloured dissolved organic matter: CDOM) resulting from these processes.

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reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are mainly collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) that simultaneously measures incident irradiance (Ed) and upwelling radiance (Lu) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) that measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II, chlorophyll fluorescence (WETStar fluorometer), conductivity, and temperature. Both instruments are deployed simultaneously to accumulate UV/VIS optical data (Ed, Lu, & Kd) while collecting discrete rosette samples at the same station for evaluation of CDOM absorption. On occassion, a Satlantic® Micro-pro UV profiling system substitutes for the SPMR.

Laboratory irradiations (both on shore and at sea) are used to quantify the efficiency of CDOM driven photochemical processes. Using a broad-spectrum 1.5 kW xenon lamp, a series of sequential long-pass optical filters, and a statistical evaluation (Rundel, 1983) of the resulting photochemical rates in 15 quartz containers, we calculate the AQY spectrum for photochemical consequences (ex. fading, CO_2 production) of CDOM reactions with a single irradiation experiment. This represents a novel approach to photochemical AQY determinations that is much faster than other monochromatic approaches (3 hrs vs. 3 weeks in some cases). This allows evaluation of both spatial and temporal variations in AQY spectra on fresh samples, not possible with other approaches. By combining spectral photochemical efficiency data, absorbance data, attenuation profiles, and solar spectral irradiance, we can calculate both whole water column and depth discriminated photochemistry.

Relationships developed using TSRB-II and SPMR data combined with discrete measurements of CDOM absorbance, allow us to combine remotely sensed data with irradiance and water optical models to estimate photochemical rates in the ocean. These data represent the beginning of regional photochemical inventories and a starting point for long-term regional scale studies of photochemical carbon transformations and CDOM dynamics in the coastal ocean.

At Dalhousie, Bill Miller (PI), Lori Ziolkowski (technician), and a graduate student, Cedric Fichot, (M.Sc.), are responsible for the ONR project, Cedric and Lori are funded full time for this effort. In 2002-2003, three cruises were used for collaboration with two projects. Two cruises were part of the Canadian SOLAS Network in the N.W. Atlantic between the Sargasso Sea and the Greenland coast, a collaboration with 15 coordinated research projects that study ocean-atmosphere exchange. The third was with D. Kieber (SUNY-Syracuse) and K. Mopper (NSF funding) for a cruise in the N.W. Atlantic along the US east coast to from RI to Wilmington, NC. This later cruise also marks year two of a collaboration with L. Martin-Traykovski and H. Sosik (WHOI: NOAA funding) to examine methods for assigning varying photochemical efficiency spectra for CO_2 production to proper water types using satellite optical data. Each field collaboration was used to collect additional optical data relevant to our ONR objectives and two included shipboard irradiations to determine photochemical AQYs.

WORK COMPLETED

We staged for and participated in three research cruises: Two in the N.W. Atlantic as part of the SOLAS project (including stations from the Scotia Shelf, the Gulf Stream, the N. Atlantic Drift, and the Subarctic Atlantic: spring bloom and summer, ~50 days total), and one along the US eastern coast

from RI to NC, adding new data from the US east coast (with Kieber et al. above). These efforts included successful completion of both laboratory irradiations and collection of *in situ* optical data.

We constructed a second water-cooled irradiation box for holding the quartz containers used during quantum yield experiments.

We produced new AQY surfaces for CDOM fading and AQY spectra for CO_2 photoproduction.

Our new algorithms, developed using over 300 stations for which we have measured *in situ* otics, were extensively extensive tested for accuracy in relating Kd in the UV to visible satellite reflectance.

We used SeaBASS optical data to independently validate our derived algorithms through rigorous match-up analysis.

We examined and compiled all optical field data collected prior to July 2002 and submitted it to WOOD.

RESULTS

We have continued to accumulate samples and optical data from diverse water types in an effort to build robust optical relationships that will be useful in predicting photochemistry from remotely sensed data. Using data amassed since the start of our ONR contract, we have modified our approach for relating Kds in the UV to satellite reflectance ratios ($Lu_{x/y}$) and used the empirical grouping of our larger optical data sets (best ratios determined using principal component analysis) and determined 3 subsets (referred to as UV provinces in Figure 1(a)) with specific fitting functions tailored to each subset. This approach improves accuracy of ag_{UV} estimates for coastal waters from remotely sensed ocean color in the visible to an average of +/- 38% with less bias than other approaches.

Figure 1 (below) shows calculated products (Kd_{320}, CDOM absorbance at 320 nm, and CDOM spectral slope coefficient (S)) from the SeaWiFS data collected during a single day over the eastern North American Atlantic coast and the Gulf of Mexico. Cedric Fichot developed this new approach as part of his thesis and regional maps of UV optical properties at all wavelengths from SeaWiFS data can be generated routinely. These optical components are required to calculate photochemical rates from remotely sensed colour. The 1000 km transect from the Delaware Bay to the Sargasso Sea (~31°N 291°W) presented in Figure 2 (below) demonstrates the type of insight into photochemical production rates possible with this approach. The vertical production of CO, calculated with our UV algorithms and previously published CO AQYs shows that coastal production occurs very close to the ocean surface which ensures ventilation to the atmosphere while open ocean production can occur at depths of 50 m, potentially allowing for consumption before ventilation. Also, surface rates are shown to vary by a factor of 5 in the surface ocean between season, driven by variations in CDOM absorbance and incident solar irradiance variations. These rates appear reasonable but field verification should follow.

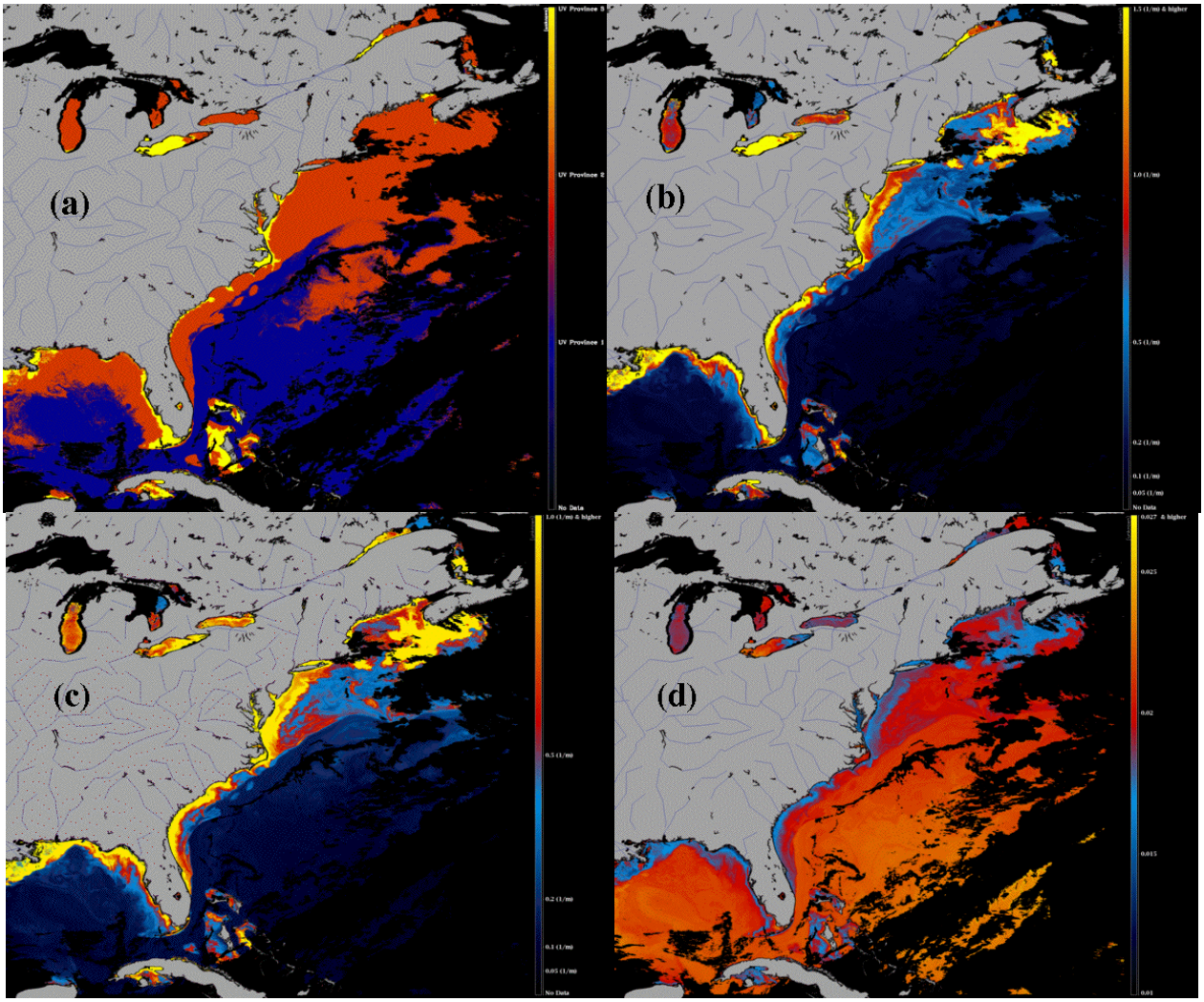

Figure 1. Mapped products from SeaWiFS data for the east coast of North America and the Gulf of Mexico (a) UV provinces and (b) total attenuation at 320nm (c) a_g320 (d) CDOM slope coefficient [Four colour images generated from SeaWiFS satellite data collected over a single day: (a) Three UV provinces as yellow (inshore), orange (coastal), and blue (oceanic) (b) calculated total attenuation at 320 nm scaled for 0.0/m as dark blue to 1.5/m as yellow (c) CDOM absorbance at 320 nm, scaled from 0.0/m as dark blue to 1.0/m as yellow, (d) spectral slope coefficient for log-linearized CDOM absorbance spectra (calculated 305-360nm), scaled from 0.01 as dark blue to 0.027 as yellow. Attenuation and CDOM absorbance show highest values in coastal regions and capture mixing fixtures in coastal and open ocean locations Slope coefficients are higher offshore.]

(b)

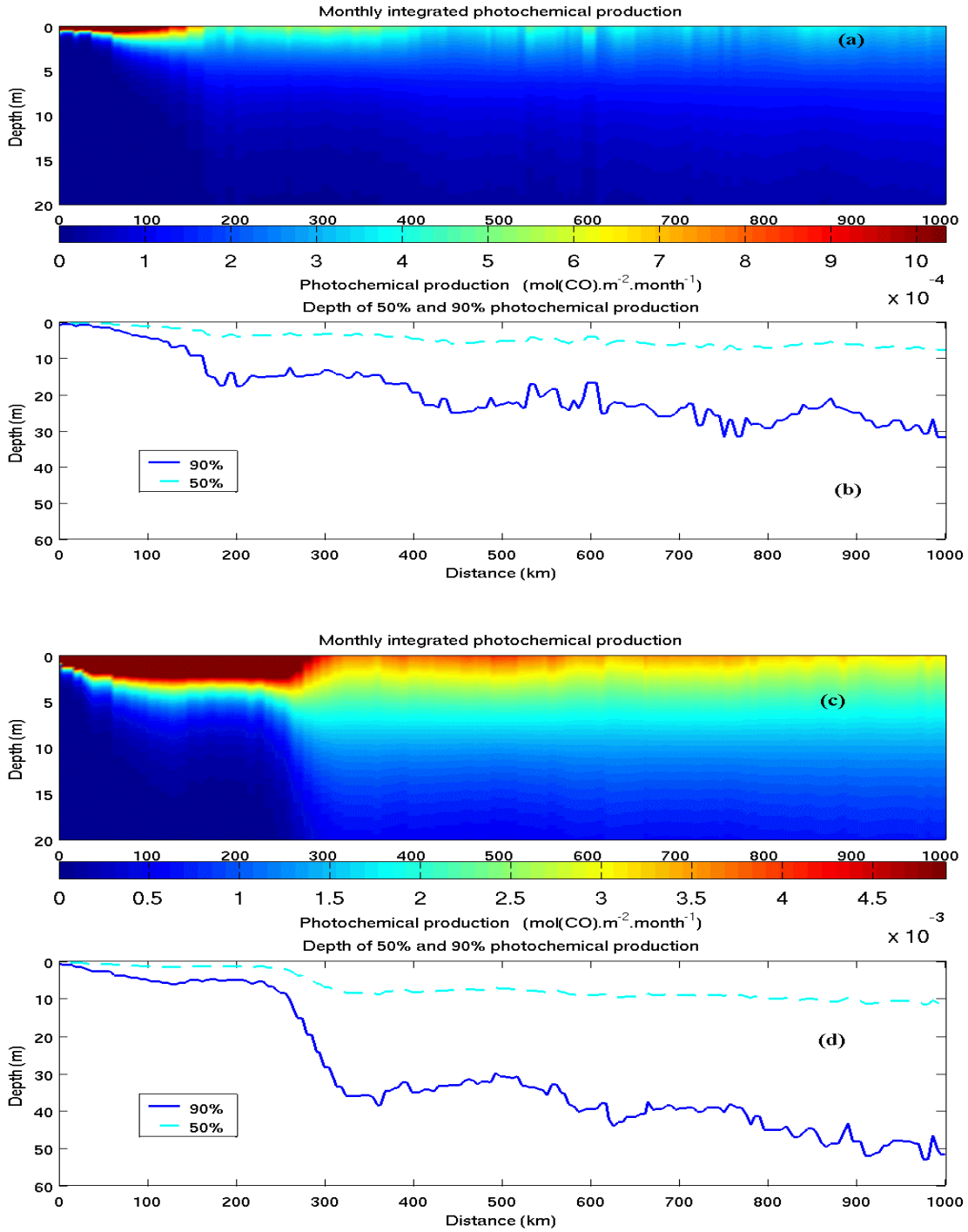

Figure 2. Simulated 1000 km transects out of the Delaware Bay into the Sargasso Sea showing vertical distribution of monthly photochemical CO production calculated from SeaWIFs data. [Four panels: Two depict the monthly vertical distribution of CO production (moles/m^2/mo) in January (a) with a colour scale from 0.0 as dark blue to 0.001 as red, and June (c) with a colour scale from 0.0 as dark blue to 0.005 as red. Two panels (b and c) show the depth of 50% (light blue dashed line) and 90%(solid blue line) CO production in winter and spring respectively. CO production is concentrated in the top 5 meters near shore and deepens across the Gulf Stream to 90% production at 50 meters in spring.]

IMPACT / APPLICATIONS

The optical properties of CDOM in the ocean control photochemical rates, effect oceanic chemical cycles, and influence the interpretation of ocean color (Miller, 1998). New algorithms allowing accurate estimation of UV attenuation from satellite data will prove invaluable to the understanding of the variability in CDOM and resulting photochemical distributions. The CDOM and photochemical distributions resulting form this approach are similar enough to field observations to argue that additional effort will produce a critical component toward predictive capability for CDOM dynamics. Better quantification of CDOM spectral shape will allow better corrections for CDOM in chlorophyll algorithms and characterization of the UV light field in the ocean. It will also result in the unique ability to address the regional and global significance of marine photochemical reactions.

TRANSITIONS

Our participation in field efforts largely result from free shiptime offered to take advantage of the UV sensors and multispectral approaches to AQY determinations developed with ONR support. Collaborators listed above are currently using novel ideas and data generated by our group with ONR support. Development of new MATLAB® algorithms (by Cedric Fichot and Lori Ziolkowski in collaboration with J.J. Cullen and R. Davis) will provide novel tools to expand quantitative evaluations of photochemistry to new groups in marine chemistry. These numerical approaches relieve many of the time constraints previously present in photochemical studies and will make spatial and temporal evaluation of CDOM dynamics feasible.

RELATED PROJECTS

Development of novel optical instrumentation proceeds in collaboration with J.J. Cullen's efforts on optical models, data analysis, and instrument development. The timely development of our Satlantic instruments and numerical modeling approaches benefits from this relationships. As stated above, we have collaborated with multiple groups on three cruises to obtain optical data, photochemical data, and the numerical relationships connecting the two. In each case, we continue to use cruises of opportunity to expand our observations and experimental data integral in our ONR objectives. The Canadian SOLAS network provides numerous opportunities for shiptime and collection of ONR relevant optical data in both the Pacific and Atlantic. SOLAS collaborates with Canadian and Japanese researchers involved in optical data sets. Our funding to participate in all but the SOLAS cruises is limited to shipping and travel costs since NSF and NOAA do not support Canadian collaborators beyond this amount. Leverage of Canadian funding of photochemical projects, however, have been used to allow expanded optical measurements that greatly benefit our ONR program.

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